UNIVERSITA' DI MESSINA
FACOLTA' DI SCIENZE

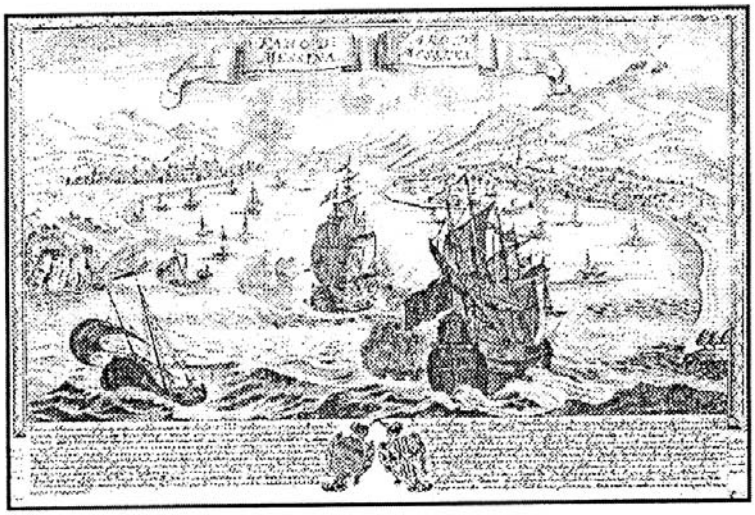
Dipartimento di Chimica Inorganica, Analititca
e Struttura Molecolare

Società Chimica Italiana
visione di Chimica Inorganica

Atti Accademia Peloritana dei Pericolanti
Classe I di Scienze Fisiche
Matematiche e Naturali

WORKSHOP ON PLATINUM CHEMISTRY

ABSTRACTS



MESSINA 30-31 MAGGIO 1994
Aula dell'Accademia

Atti Accademia Peloritana dei Pericolanti
Classe I di Scienze Fis. Mat. e Nat.
Vol. LXXII (1994) - Convegno 30-31 maggio 1994

PERSPECTIVES IN SQUARE PLANAR SUBSTITUTION REACTIONS

L. CATTALINI

The general behaviour of platinum(II) complexes undergoing nucleophilic substitution of the coordinated ligands has been established since several years ago. The normal mechanism can be described as an asychronous associative substitution even if examples of dissociative mechanism are known. A sequence of reactivity has been established and more or less confirmed with a large number of substrates. A limited amount of data exist about the trans and cis kinetic effects and steric restrictions to substitution, and some case has been reported of "anchimeric assistence" and "electrophilic catalysis".

To predict new studies in this area is just a matter of phantasy. However, a number of points of interest are already clear.

A possibility exist to investigate more nucleophiles, on building up appropriate substrates and systems; mention can be made to oxygen donors (the nucleophilicity of hydroxide is still a matter of discussion), many sulphur donors, ion pairs and triplets, cationic donors, metal complexes acting as nucleophiles or producing electrophilic catalysis to nucleophilic substitution.

Synthetic aspects are obviously related to this subject.

Also the amount of data concerning different classes of leaving groups is limited and it may be of interest to investigate systems where strong donors such as phosphines and arsines undergo nucleophilic displacement. In a number of cases the problem seems to be more thermodynamic than kinetic, i.e. conditions have to be found to force the equilibria to the desired direction.

An open area is that concerning polynuclear complexes, from the study of bridge splitting reactions to that of the reactivity of bimetallic systems. Recent developments in the synthesis of new possible substrates (such as the "A-shaped" dimers) offer a number of possibilities. With an adequate instrumentation it may be of interest to apply the kinetic methods to investigate heterogeneous systems, such as those provided by resins containing the reactive substrates. Also the study of the role of an increasing steric hindrance on the reaction mechanism(s) would be of relevant interest.

Finally, a thema which can be developed is the use of kinetic tools to acquire more and precise knowledge of the chemicals bonds. An example will be presented.

Università di Venezia
Dipartimento di Chimica

Atti Accademia Peloritana dei Pericolanti
Classe I di Scienze Fis. Mat. e Nat.
Vol. LXXII (1994) - Convegno 30-31 maggio 1994

NON-ISOTHERMAL SPECTROPHOTOMETRIC KINETICS APPLIED TO INORGANIC REACTIONS

GIUSEPPE ALIBRANDI

A method based on non-isothermal analisys[1] has been used to obtain kinetic constants and activation parameters of some inorganic reactions in solution. The main feature of the method is to change the way of producing the kinetic data. Instead of obtaining single values of rate constants at single different temperatures, the aim is to produce in a single short experiment a $k(T)$ profile (i.e. a whole set of rate constants in a definite temperature range).

The reactions studied under various experimental conditions to test the method were the thermal decomposition of the alkyl solvento species *trans*-$[Pt(PEt_3)_2(n\text{-}C_4H_9)(CH_3OH)]^+$ to yield the *trans*-hydride $[Pt(PEt_3)_2(H)(CH_3OH)]^+$ in methanol[2] and the cis-trans isomerization of the cation $[Pt(PEt_3)_2(CH_3)(C_2H_5OH)]^+$ in ethanol.[3]

Experiments were carried out collecting by a computer the values of the absorbance of the reaction mixture while increasing the temperature in a linear way (Fig. 1). The absorbance-time

data collected were then processed by appropriate algorithms using both differential and integral methods to obtain the $k(T)$ profile (Fig. 2). In the integral method a direct best fitting to equation (1) was performed with D_0, D_∞, $\Delta H^{\neq}$ and $\Delta S^{\neq}$ as the parameters to be optimized.

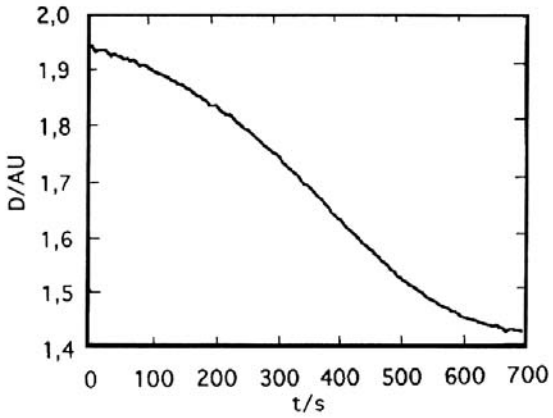


Figura 1

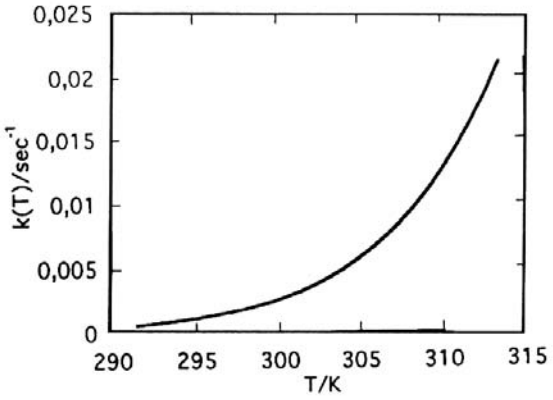


Figura 2

$$(1) \quad D_t = (D_0 - D_\infty e^{\left\{ -\frac{k}{h} e^{\left[\frac{\Delta S^{\neq}}{R}\right]} \int_0^t (T_0+\alpha t) e^{\left[-\frac{\Delta H^{\neq}}{R(T_0+\alpha t)}\right]} dr \right\}} + D_\infty$$

The activation parameters $\Delta H^{\neq}$ and $\Delta S^{\neq}$ have very low statistical errors and are comparable with those obtained by the traditional isothermal method, where the error is greater.

For non-unimolecular reactions carried out under pseudo-first-order conditions (e.g. a nucleophilic substitution reaction on a square planar complex, where $k_{obs} = k_1 + k_2[Y]$) the $k(T)$ profile becomes a $k_{obs}(T)$ profile containing different contributions. In such cases it is necessary to perform the usual analysis of the dependence of k_{obs} on the concentration of all of the reagents that now can be made in the whole temperature range by a global fitting. A number of these cases are under investigation.

REFERENCES

[1] E. Koch, *Non-isothermal Reaction Analysis*, Academic Press, London, 1977 and References therein.

[2] R. Romeo, G. Alibrandi and L. Monsù Scolaro, *Inorg, Chem., 32* **(1993)** 4688.

[3] G. Alibrandi, D. Minniti, L. Monsù Scolaro and R. Romeo, *Inorg, Chem., 27* **(1988)** 318.

Dipartimento di Chimica Inorganica
Analitica e Struttura Molecolare
Università di Messina, Salita Sperone 31
Vill. S. Agata, 98166 Messina, Italy